Preparation and Electrochemical Performance of Fe$_3$O$_4$-SWCNTs/ionic Liquid Nanocomposites as Sensor for Determination of Tert-Butylhydroquinone

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In this research, electro-catalytic activity of paste electrode (PE) modified with Fe$_3$O$_4$-SWCNTs and 1-Hexyl-3-methylimidazolium tetrafluoroborate (1H3MITFB) nanocomposites toward the oxidation of tert-butylhydroquinone (TBHQ), was investigated. The results showed that Fe$_3$O$_4$-SWCNTs/1H3MITFB/PE could improve the oxidation current of TBHQ up to about 3.65 times under the optimum condition. On the other hand, oxidation behavior of TBHQ was shown to have a linear relationship with pH of solution with a negative slope (55.2 mV/pH), confirming the presence of two electrons and two protons in redox reaction of this food additive. SW voltammograms of TBHQ at the surface of Fe$_3$O$_4$-SWCNTs/1H3MITFB/PE displayed a linear relationship in concentration range of 0.008 to 350 µM with the detection limit of 2.0 nM. The standard addition results showed that Fe$_3$O$_4$-SWCNTs/1H3MITFB/PE could be used as a powerful analytical approach to determine TBHQ in food samples.

Keyword: Tert-butylhydroquinone, Food sensor, Fe$_3$O$_4$-SWCNTs nanocomposite, Ionic liquid

1. INTRODUCTION

Determining food additives, especially antioxidants, is one of the most important issues in investigating food quality products [1]. Due to the side effects of the excessive consumption of synthetic antioxidants in food products, the measurement of antioxidants concentrations in food products has become an important subject in food industry. Therefore, analytical strategies were suggested for the determination of food additives since many years ago [2-5].
Tert-butylhydroquinone is one of the famous phenolic antioxidants with a wide range application in frozen fish, fish fillet, fish products, and animal-derived food products as well as in fats or oils with an acceptable value of 1000 mg/kg [6]. National Library of Medicine (NLM) confirmed that TBHQ causes convulsions, neurotoxic effects, liver enlargement, and paralysis in laboratory animals. Due to the above-mentioned points and the widespread use of TBHQ in food industry, estimating the concentration of this antioxidant in food samples has become particularly important, especially for evaluating the quality of food products [7].

Among the analytical approaches suggested for TBHQ analysis, electrochemical methods have received more attention compared to other techniques [8]. This can be due to the electrochemical sensors more advantages such as high analysis speed and the ability to modify electrochemical sensors properly for the selective measurement of pharmaceutical and food compounds [9-20]. On the other hand, a wide range application of mediators in the modification process and their synergic effect on the modification process create a high sensitivity condition for the fabrication of new types of electrochemical sensors [21-30].

Nano-based compounds created a new attitude to materials science and surprised science with their unique properties [31-45]. Due to the extraordinary properties of nanomaterials, they were rapidly applied in various branches of science [46-61]. Accordingly, high electrical conductivity of nanomaterials is one of their unique features, which makes them a suitable option for making electrochemical sensors [62-77].

Ionic liquid is one of organic solvents with high conductivity and suitable catalytic effect that can create an amplification on electrochemical sensors for trace level’s analysis [78-81].

In this research, Fe3O4-SWCNTs/1H3MITFB/PE was introduced as a new powerful sensor for the nanomolar determination of TBHQ in food samples. According to I-V results, the Fe3O4-SWCNTs/1H3MITFB/PE was successfully used for the determination of TBHQ in foods produced with acceptable recovery data.

2. EXPERIMENTAL

2.1. Materials and instruments

Tert-butylhydroquinone, iron (III) chloride, SWCNTs-COOH, iron (II) sulfate, sodium hydroxide, 1-hexyl-3-methylimidazolium tetrafluoroborate, graphite powder, phosphoric acid, paraffin oil and hydrochloric acid were purchased from Sigma and Merck Company. Stock solution of TBHQ (0.01 M) used in this study was prepared by dissolving 0.0166 g TBHQ into 10 mL phosphate buffer solution (PBS) pH=7.0. Thereafter, I-V curves were recorded using a µ-Autolab instrument connected to three electrodes cells. Ag/AgCl/KCl was used as the reference electrode in I-V investigations. Fe3O4-SWCNTs was synthesized using a simple precipitation method reported in a study by Emamian et al [82].
2.2. Preparation of Fe₃O₄-SWCNTs/1H3MITFB/PE

The 0.96 g graphite powder + 0.04 g Fe₃O₄-SWCNTs was mixed with hand in the presence of 8 drops of paraffin oil as well as 2 drops of 1H3MITFB for the fabrication of Fe₃O₄-SWCNTs/1H3MITFB/PE into mortar and pestle. The obtained paste was put at the end of glass tube, and copper wire was then used for electrical conductivity.

2.3. Preparation of real sample

Drinking water and apple juice were purchased from local market and then centrifuge for 30 min at 300 rpm. The obtained juice was diluted by PBS (pH=4.0) and then used for real sample analysis.

3. RESULTS AND DISCUSSION

3.1. Fe₃O₄-SWCNTs characterization

The Fe₃O₄-SWCNTs nanocomposite was characterized by FESEM method. The FESEM image of Fe₃O₄-SWCNTs nanocomposite clearly confirmed the decoration of Fe₃O₄ nanoparticle at surface of SWCNTs with a good distribution.

![FESEM image of Fe₃O₄-SWCNTs composite](image)

**Figure 1.** FESEM image of Fe₃O₄-SWCNTs composite

3.2. Electrochemical behavior

The relationship between oxidation signal of TBHQ and changes in pH was investigated in this step. For this goal, square wave voltammograms (SWV) of 120 µM TBHQ was recorded in the pH range
of 4.0 to 8.0 (Figure 2). The results displayed a linear relationship between the potential and pH in this pH range with slope of 55.2 mV/pH that confirmed the suggested mechanism, which is reported in scheme 1 with equal value of electron and proton [21]. According to SW voltammograms, the maximum oxidation current for TBHQ was observed at pH=7.0 and this value was selected for next steps.

![Figure 2](image2.png)

**Figure 2.** E-pH curve for electro-oxidation of 120 µM TBHQ. Inset) SW voltammograms of 120 µM TBHQ in the different pH range.

![Scheme 1](image1.png)

**Scheme 1.** TBHQ electro-oxidation mechanism
Figure 3. SW voltammogram of 120 µM TBHQ at surface of a) PE, b) Fe$_3$O$_4$-SWCNTs/PE, c) 1H3MITFB/PE and d) Fe$_3$O$_4$-SWCNTs/1H3MITFB/PE

Figure 4. I- ν$^{1/2}$ curve for electro-oxidation 500 µM TBHQ at scan rates a) 10, b) 50, c) 100 and d) 150 mV/s.
The catalytic activity of Fe$_3$O$_4$-SWCNTs/1H3MITFB/PE on oxidation signal of TBHQ was investigated by recording square wave voltammograms of 120 µM TBHQ at the surface of PE (figure 3 curve a), Fe$_3$O$_4$-SWCNTs/PE (figure 3 curve b), 1H3MITFB/PE (figure 3 curve c) and Fe$_3$O$_4$-SWCNTs/1H3MITFB/PE (figure 3 curve d).

According to the recorded voltammograms, by moving PE to Fe$_3$O$_4$-SWCNTs/1H3MITFB/PE, the oxidation current of TBHQ has increased from 10.8 µA to 39.5 µA confirming the catalytic activities of Fe$_3$O$_4$-SWCNTs and 1H3MITFB after the modification of PE. This point confirm catalytic activity of nanomaterials and ionic liquids for modification of sensors [83-87].

In this study, a linear relationship was detected between the oxidation currents of TBHQ vs. $\nu^{1/2}$ using the linear sweep voltammetric method (Figure 4). This relation confirm diffusion process [88-95] for electro-oxidation of TBHQ at surface of Fe$_3$O$_4$-SWCNTs/1H3MITFB/PE.

The SW voltammograms of TBHQ showed a linear relation with its concentration ($I = 0.3321 C + 2.4706; R^2 = 0.9967$) in the range 0.008-350 µM using Fe$_3$O$_4$-SWCNTs/1H3MITFB/PE as working sensor. The Fe$_3$O$_4$-SWCNTs/1H3MITFB/PE showed a detection limit 2.0 nM for determination of TBHQ in aqueous solution. The values of LDR and LOD is comparable with previous suggested sensor for determination of TBHQ (Table 1) [96-99].

Figure 5. I-C curve for electro-oxidation of TBHQ. Insert) SW voltammograms of TBHQ in the concentration range a) 0.008; b) 1.0; c) 15.0; d) 40.0; e) 60.0; f) 80.0; g) 120.0; h) 180.0; i) 250; j) 300 and k) 350 µM.
Table 1. Analytical data relative to suggested sensors for determination of TBHQ.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Mediator</th>
<th>LDR (µM)</th>
<th>LOD (µM)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPE</td>
<td>3D reduced graphene oxide/FeNi3-ionic liquid nanocomposite</td>
<td>0.05-900.0</td>
<td>0.01</td>
<td>[96]</td>
</tr>
<tr>
<td>CPE</td>
<td>cetyltrimethylammonium bromide</td>
<td>1.05-10.15</td>
<td>0.078</td>
<td>[97]</td>
</tr>
<tr>
<td>Pt disk ultramicroelectrode</td>
<td>Not modification</td>
<td>1200 - 3900</td>
<td>170</td>
<td>[98]</td>
</tr>
<tr>
<td>Gold electrode</td>
<td>Multiwalled carbon nanotube</td>
<td>4.0 - 100</td>
<td>0.032</td>
<td>[99]</td>
</tr>
<tr>
<td>CPE</td>
<td>Fe$_3$O$_4$-SWCNTs/1H3MITFB</td>
<td>0.008-350</td>
<td>0.002</td>
<td>This work</td>
</tr>
</tbody>
</table>

The interference study showed that Fe$_3$O$_4$-SWCNTs/1H3MITFB/PE could be used as powerful sensor for determination of TBHQ in food products. Results showed presence additives in food samples such as vitamins donot show any important interference for determination of 20 µM TBHQ at pH=7.0 (Table 2).

Table 2. The selectivity results of Fe$_3$O$_4$-SWCNTs/1H3MITFB/PE for determination of 20 µM TBHQ.

<table>
<thead>
<tr>
<th>Species</th>
<th>Tolerant limits (W$<em>{interference}$/W$</em>{TBHQ}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_3^-$, K$^+$, Br$^-$, F$^-$, Ca$^{2+}$</td>
<td>1000</td>
</tr>
<tr>
<td>Vitamin B$_{12}$, Vitamin B$_9$ and methionine</td>
<td>750</td>
</tr>
<tr>
<td>Glucose</td>
<td>600</td>
</tr>
</tbody>
</table>

On the other hand, ability of Fe$_3$O$_4$-SWCNTs/1H3MITFB/PE for determination of TBHQ was check by standard addition method. Results are presence in Table 3 and recovery data confirm powerful ability Fe$_3$O$_4$-SWCNTs/1H3MITFB/PE for determination of TBHQ in real sample.

Table 3. Determination of TBHQ using Fe$_3$O$_4$-SWCNTs/1H3MITFB/PE in food samples (n=5)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Exist (µM)</th>
<th>Found (µM)</th>
<th>Recovery%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drinking water</td>
<td>---</td>
<td>&lt;LOD</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>10.00</td>
<td>9.73±0.55</td>
<td>97.3</td>
</tr>
<tr>
<td>Appel juices</td>
<td>---</td>
<td>&lt;LOD</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.00</td>
<td>10.46±0.74</td>
<td>104.6</td>
</tr>
</tbody>
</table>

In the final step, stability of Fe$_3$O$_4$-SWCNTs/1H3MITFB/PE was check in period time two month. After two month, 91.8% of its initial oxidation current was remained that confirm good stability of Fe$_3$O$_4$-SWCNTs/1H3MITFB/PE as new sensor.
4. CONCLUSION

A highly sensitive and simple food electrochemical sensor was fabricated for determination of TBHQ in food products. The Fe₃O₄-SWCNTs/1H3MITFB/PE showed good electro-catalytic activity toward oxidation of TBHQ at pH=7.0 as optimum condition. The SW investigation confirm ability of Fe₃O₄-SWCNTs/1H3MITFB/PE for determination of TBHQ in concentration range 0.008-350 µM with detection limit 2.0 nM. The Fe₃O₄-SWCNTs/1H3MITFB/PE showed powerful ability as sensor for determination of TBHQ in food products such as drinking water and apple juice samples.

References

55. E. Vatandost, A. Ghorbani-HasanSaraei, F. Chekin, S-A. Shahidi, S. Naghizadeh Raeisi,


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